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Development of a Mass Balance Model for Estimating PCB Export from the Lower Fox River to Green Bay

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ABSTRACT. *A mass balance approach was used to model contaminant cycling in the lower Fox River from the DePere Dam to Green Bay. The objectives of this research were 1) to estimate present contaminant export from the Fox River to Green Bay, and 2) to quantify contaminant transport and fate pathways in the lower river for the study period. Specifically, a model describing the transport, fate, and export of chlorides, total suspended solids, total PCBs, and six PCB congeners for the lower Fox River was developed. Field data collected as part of the U.S. Environmental Protection Agency's Green Bay Mass Balance Study were used to calibrate the model. From 10 October 1988 to 31 May 1990, the estimated total PCB export was 423 kg; for calendar year 1989, the estimate was 280 kg. Model results suggest that the transport of in-place pollutants significantly contributed to the cumulative export of total PCBs over this period. Estimated total PCB transport in the Fox River during 1989 increased 60% between the dam and river mouth due to the resuspension of lower river sediments. Total suspended solids and PCB predictions are most sensitive to particle transport parameters, particularly the settling and resuspension velocities. The significant components of the total PCB mass balance are import (loading over the DePere Dam), settling, resuspension, and export to Green Bay. Volatilization, porewater transport, and point source input were not significant to the mass balance. Present point source discharges to the river are not significant total PCB sources, collectively contributing less than 6 kg of PCB to the river during the mass balance period.*

INDEX WORDS: *Fox River, mathematical model, PCBs, mass balance, Lake Michigan, resuspended solids.*

INTRODUCTION

Green Bay has long been recognized as a region adversely impacted by the input of anthropogenic contaminants. The southern portion of the bay and the lower Fox River suffer from a variety of water quality problems and are an International Joint Commission (IJC) Area of Concern (AOC). The IJC designation is due, in part, to extensive contamination by polychlorinated biphenyls (PCBs). The Fox River is the largest tributary to Green Bay and also the largest source of PCBs (Swackhamer and Armstrong 1987, Marti and Armstrong 1990). The discharge of PCBs from paper recycling mills in the basin resulted in the contamination of the sediments, water column, and biota of the Fox River and the adjacent areas of Green Bay. Although their use and manufacture have been banned, significant quantities of PCBs continue to be exported to Green Bay from the Fox River. Consequently, the Fox River is a primary focus when considering possible control options for PCB contamination of the Green Bay AOC.

The lower Fox River was studied as part of the 1989 Green Bay Mass Balance Study (GBMBS) (USEPA 1989). The purpose of the GBMBS was to demonstrate the mass balance approach for managing toxic chemicals in the Great Lakes. A primary goal was to measure PCB inputs and fluxes from all direct and diffuse sources, including point source discharges, the atmosphere, sediments, tributaries, runoff, groundwater, landfills, etc., to identify the most significant PCB sources as a basis for taking effective remedial actions. Therefore, the GBMBS focused on the sources, transport, and fate of PCBs from the upper Fox River boundary with Lake Winnebago, through the lower Fox River, and into Green Bay, as well as accumulation in the aquatic food web of the lower river and bay. With respect to the lower Fox River component of the study, a mass balance water quality model was developed with the objectives of 1) estimating present PCB export (tributary loading) from the Fox River to Green Bay, and 2) simulate and quantify PCB transport and fate pathways in the lower river.

LOWER FOX RIVER SITE DESCRIPTION

Located in the State of Wisconsin, the Fox River is the largest tributary to Green Bay. The Fox River has a drainage basin of over 17,000 km^2, and its flow is regulated by a series of dams. The upstream boundary for the lower Fox River study area was the DePere Dam, located approximately 11 km upstream of the river mouth. The downstream boundary was Little Tail Point, located 12 km beyond the river mouth. Within these boundaries, three small tributaries join the Fox River. Also within these boundaries are seven major industrial and municipal point source dischargers. Water quality monitoring stations were established at each point source, the DePere Dam, five locations in the river between the dam and the mouth (stations 51-55), the Fox River mouth, and 27 locations in Green Bay (Fig. 1). The locations of the monitoring stations in Green Bay are not shown.

MODEL DEVELOPMENT

The lower Fox River water quality model is comprised of three major components: transport within the water column, sediment transport, and contaminant transport and fate. Chlorides and total suspended solids (TSS) were used to develop and

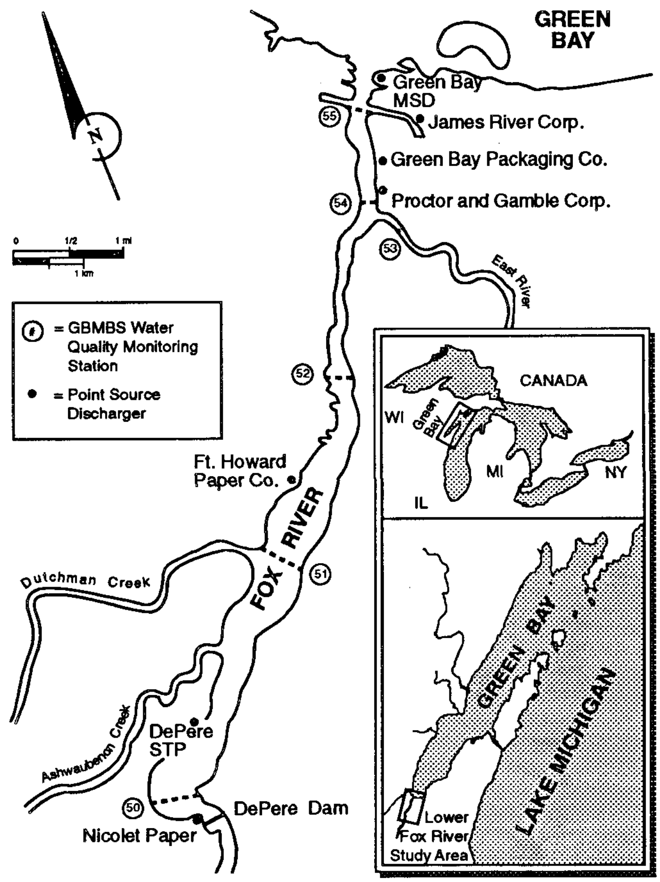

FIG. 1. Lower Fox River study area.

calibrate the water column and sediment transport components of the model, respectively. Total PCBs (computed as the sum of PCB congeners, ΣPCBs) were the contaminant of central interest and were used to develop and calibrate the contaminant transport component of the model. Six PCB congeners were also modeled to verify the calibration. The temporal scale of the model was daily to weekly for all model inputs and results. The lower Fox River mass balance project report provides detailed and complete descriptions of all aspects of the model development (Velleux *et al.* 1992).

The transport and fate processes included in the lower Fox River model are: advection, dispersion, settling, resuspension, burial, sediment porewater advection and diffusion, three-phase partitioning, volatilization, and external loadings (Fig. 2). It was assumed that sediment decomposition was negligible because reported biochemical decay rates (Walker and Snodgrass 1986) are much smaller than particle transport rates. It was also assumed that PCB degra-

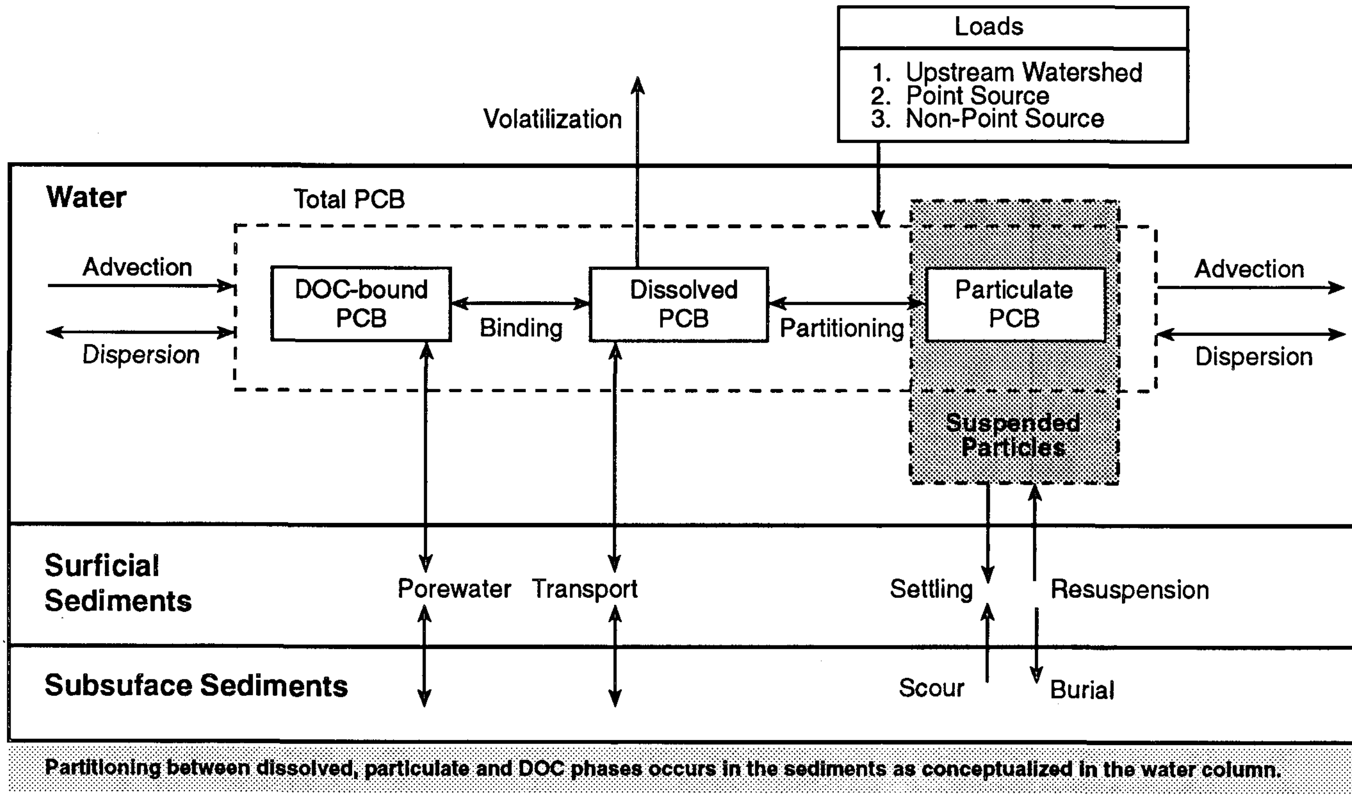

FIG. 2. Lower Fox River conceptual model framework.

dation was negligible over the mass balance period for the PCB concentrations present in lower Fox River sediments (Quensen *et al.* 1988, Rhee *et al.* 1993). From this conceptual framework, dynamic mass balance equations for the lower Fox River were developed. These equations define quantitative relationships between material inputs (loadings) and water quality (concentration). To simplify the numerical solution of these expressions, three conventional assumptions were made (Thomann 1972, Chapra and Reckhow 1983, Thomann and Mueller 1987): 1) water column and sediment volumes do not change during an integration time interval; 2) sediments do not move horizontally (no bed load); and 3) ΣPCB partitioning to solids and dissolved organic materials is rapid relative to other processes (local equilibrium). The resulting ordinary differential equations for the water column and sediments mass balance and the finite difference approximations that define the model are extensively documented (Di Toro *et al.* 1982, Richardson *et al.* 1983; Thomann and Mueller 1987; O'Connor 1988a, 1988b).

A modified version of TOXI4, one of the WASP4 model frameworks, was the computational framework for the lower Fox River application (Ambrose *et al.* 1988, Freeman and Endicott 1990, Freeman *et al.* 1992). The framework was modified to simplify the simulation of a single solids type. With these revisions, the settling and resuspension velocities are input and the gross settling and resuspension fluxes computed. Over short time scales, the depth (thickness) of the surficial sediment layer is allowed to vary in response to the difference between settling and resuspension. Over longer time scales, burial is internally computed from the difference between the settling and resuspension fluxes. For the application of TOXI4 to systems subject to significant deposition and resuspension events, such as the Fox River, these modifications substantially improve the framework.

The lower Fox River model system was divided into 126 segments in five layers: water column, surficial sediments, and three subsurface sediment layers (Fig. 3). In the water column, there are sixteen

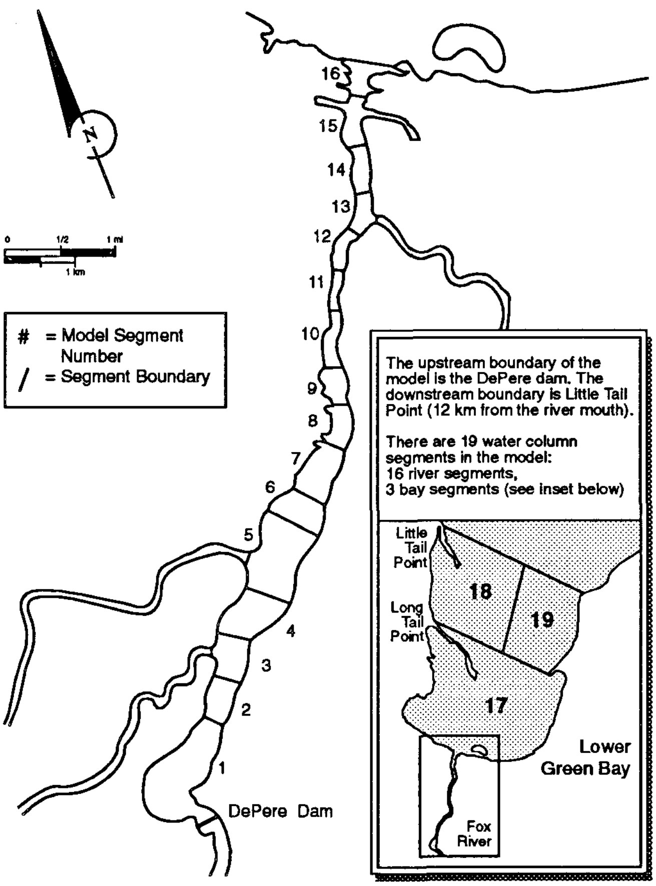

FIG. 3. Lower Fox River model segmentation.

segments in the river proper, from the DePere Dam to the river mouth, and three additional segments in the inner bay. The inner bay segments serve to minimize the effects of specified boundary conditions. In the sediments, two segment types, net erosional and net depositional, were defined beneath each water column segment in the river for the surficial and upper two subsurface sediment layers. This distinction was based on sediment transport computations and bathymetric measurements suggesting that, during high flow events, significant erosion is confined to deeper, mid-channel river sediments while nearshore sediments are not eroded (Gailani *et al.* 1991, Gailani *et al.* 1993). Segment morphometry was estimated from National Oceanic and Atmospheric Administration (NOAA) navigational charts and U.S. Army Corps of Engineers dredging maps. Vertical sediment segmentation was based on sediment core data collected as part of the GBMBS. A surficial sediment layer thickness of 10 cm and subsurface sediment layer thicknesses of 20, 120, and 150 cm were selected on the basis of ΣPCB concentration profiles observed in the sediment core data.

The mass balance period was 10 October 1988 to 31 May 1990. During this period field data for each water quality monitoring station were collected. Additional data describing contaminant concentrations and spatial distributions in the sediments of the river were also collected. These data, in conjunction with the parameter estimation and calibration methods described in the following section, were used to parameterize the lower Fox River model and also served as the basis for evaluating model performance.

FIELD DATA ANALYSIS AND PARAMETER ESTIMATION

A number of agencies contributed to data collection efforts during the GBMBS, each using a different sample collection and analytical protocol (Table 1). The U.S. Geological Survey (USGS) collected field samples at the DePere Dam and the Fox River mouth. The U.S. EPA Great Lakes National Program Office (GLNPO) collected samples at the in-river monitoring stations and in Green Bay during eight mass balance cruises. The Wisconsin Department of Natural Resources (WDNR) collected influent and effluent samples for each point source discharger. Before these data were used to calibrate the model, an effort was made to ensure that the field data were comparable. When data were not directly comparable due to differences in the sampling and analytical procedures, adjustments were developed to allow intercomparisons of the various data sets. The Green Bay/Fox River mass balance study plan provides a more detailed description of the GBMBS sampling plan and protocols (USEPA 1989).

Field data comparability was evaluated by graphical and statistical comparisons of data sets as well as by consideration of the sample collection, compositing, filtration, and analytical procedures. The chloride field data were relatively comparable and did not require adjustment as the differences caused by differing spatial and temporal compositing schemes for each data set appeared minimal. The solids field data resulted from a heterogeneous mix of sample collection and analytical protocols. These data required adjustment for differences between the spatial and temporal sample collection protocols as well as analytical procedures to

TABLE 1. Agencies contributing to GBMBS field data collection efforts.

Agency	Station	Constituent	Collection	Analysis/Filtration
USGS	DePere	Flow	Stage Height	Rating Curve
		Chlorides	ISCO	Chlorides (Cl)
		Chlorides	EWI	Chlorides (Cl)
		Solids	ISCO	Suspended sediments (SS):1.6 μm
		Solids	ISCO	Total suspended solids (TSS):1.6 μm
		Solids	ISCO	Total suspended solids (TSS):0.7 μm
		Solids	EWI	Total suspended solids (TSS):0.7 μm
		OC	EWI	Dissolved and Particulate Organic Carbon: 0.7 μm
		PCBs	EWI	Dissolved and Particulate PCB Congeners: 0.7 μm
	Mouth	Chlorides	ISCO	Chlorides (Cl)
		Chlorides	EWI	Chlorides (Cl)
		Solids	ISCO	Suspended sediments:1.6 μm
		Solids	ISCO	Total suspended solids (TSS):1.6 μm
		Solids	ISCO	Total suspended solids (TSS):0.7 μm
		Solids	EWI	Total suspended solids (TSS):0.7 μm
		OC	EWI	Dissolved and particulate Organic Carbon
		PCBs	EWI	Dissolved and Particulate PCB Congeners: 0.7 μm
GLNPO	50-55/Bay	Chlorides	Cruise	Chlorides (Cl)
		Solids	Cruise	Total suspended solids (TSS):0.7 μm
		OC	Cruise	Total and dissolved Organic Carbon
		PCBs	Cruise	Dissolved and Particulate PCB Congeners: 0.7 μm
WDNR	Pt. Source	Chlorides	Effluent	Chlorides (Cl)
		Solids	Effluent	Total suspended solids (TSS)
		PCBs	Effluent	Total PCB Congeners
	Nonpoint	Solids	Estimated	Nonpoint runoff/Land use
	Sediments	Solids	Gravity Core	% Dry Matter; % Sand, Silt, Clay
		PCBs	Gravity Core	20% PCB Congeners; 80% Total PCB
NOAA	Green Bay	Wind	Wind Gauge	Wind speed and direction

PCB samples collected by the USGS and WDNR were analyzed at the Wisconsin State Laboratory of Hygiene; PCB samples collected by GLNPO were analyzed at the University of Minnesota-Duluth. ISCO samples were 24-hour composites collected using an ISCO automatic sampling device; EWI samples were collected from a boat using an equal width increment sampling technique. Filtration indicates nominal filter pore size. Data provided courtesy of GBMBS principal investigators.

improve data comparability (Velleux *et al.* 1992). The PCB field data, in contrast, were collected and analyzed by more consistent sample collection and analytical protocols. Congener specific analyses were performed on each water column and point source sample analyzed for PCBs. Total PCB concentrations were computed as the sum of the congener values (ΣPCB). Differences in spatial and temporal compositing schemes that existed between data sets were not completely resolvable (Velleux *et al.* 1992). Field data collected at the Fox River mouth were also adjusted for seiche influence to account for "ebb tide" sampling bias (Velleux *et al.* 1992). The WDNR point source data, although sparse, were appropriate for estimating point source chloride and TSS loads without adjustment. However, the WDNR data were inappropriate for directly estimating point source ΣPCB loads and required specialized analysis (described below).

Daily flows in the lower Fox River were measured at the DePere Dam and used to parameterize advection in the river. Advection in the inner bay was based on the results of the Green Bay water quality model developed as part of the GBMBS (Bierman *et al.* 1992). Porewater advection was estimated from seepage measurements (determined from electrical conductance) and the results of a regional groundwater flow model for the Fox River/Green Bay area (Cherkauer and Taylor 1992).

Estimating the loading of chloride, TSS, and PCBs over the DePere Dam was a critical element of the field data analysis for model development because upstream loading was a major component of the mass balance for each constituent. Upstream chloride loads were estimated from a regression analysis of chloride concentration and daily flow observations. TSS loads were estimated directly from TSS concentration and flow observations; no regression analysis was required. ΣPCB loads were estimated from separate regression analyses of dissolved (dΣPCB) and particulate ΣPCB (pΣPCB) concentrations with TSS and flow observations. For each contaminant, daily upstream loads were computed as the product of the flow and concentration observations (if available) or the regression estimates (Table 2).

Point source chloride and TSS loads were estimated from concentration and discharge data collected for each discharger. Point source ΣPCB loads were also estimated from ΣPCB concentration and daily discharge data. The point source PCB congener data were heavily censored. More than 80% of the data were reported as either below the detection limit or unquantified due to analytical interferences. Consequently, it was necessary to estimate replacement values for the censored data in order to compute unbiased PCB concentrations and loads. A maximum likelihood estimator (MLE) procedure was developed and used to compute replacement values (Helsel 1990, Dolan and El-Shaarawi 1991, Freeman *et al.* 1993). Congener concentrations were summed for each sample using the observed concentrations or MLE replacement values (for data reported below the detection limit) and ΣPCB loads computed.

Other solids sources considered in the TSS mass balance were autochthonous (internal) production and nonpoint loading. Autochthonous solids production was estimated from historical productivity data (Auer 1984) and light extinction data (Conley 1983) following the procedure described by Raghunathan (Raghunathan 1990) and accounted for 5% of the cumulative solids load to the river and inner bay. The WDNR evaluated land use practices and runoff in the lower Fox River and East River watersheds to estimate nonpoint solids loadings (WDNR 1991). Nonpoint TSS loads from the East River watershed accounted for another 5% of the cumulative solids load to the river. Nonpoint TSS loads that enter the river between the DePere Dam and river mouth accounted for less than 1% of the cumulative TSS load to the river and were not considered in the mass balance. Nonpoint, landfill, and groundwater PCB sources along the lower Fox River were assessed as part of the GBMBS and found to be negligible.

Downstream boundary conditions were estimated from concentration data collected in the inner portion of Green Bay (stations 9–12). For the water column segments defining the "downstream" limit of the model (segments 18 and 19), the time series of chloride, TSS, and ΣPCB data collected at these water quality monitoring stations were used to establish boundary conditions. On days for which no data were available, boundary conditions were estimated by linear interpolation between available data points.

Sediment ΣPCB initial conditions and inventory were estimated from data for samples of 68 sediment cores collected in the lower Fox River. PCB congener analyses were performed on 20% of the samples and total PCB analyses performed on the remaining 80%. Total organic carbon, % dry matter, and particle size distribution were also mea-

TABLE 2. Lower Fox River upstream load estimation methods and results.

Contaminant	Estimation method	r^2	p value	n
Chloride	Polynomial Regression	0.56	<0.05	119
TSS	Direct (Observed Q × C)	-	-	473
ΣPCB	Multiple Linear Regression	dΣPCB: 0.46 pΣPCB: 0.75	<0.05 <0.05	47 47
PCB Congener:	Multiple Linear Regression		<0.05	47
28+31		0.652		
56+60		0.746		
101		0.751		
138+158+163		0.800		
149		0.844		
180		0.709		

sured. The data were segregated by location and zone (net erosional or net depositional) and a 3-dimensional interpolation was created for the data in each zone using the GMP software package (Dynamic Graphics, Inc. 1992). Initial conditions for each sediment segment were then established by visual examination of the 3-D interpolations of the field data. Sediment ΣPCB inventory was computed as the products of the initial concentrations and segment volumes, summed over the river sediment segments.

Partitioning was treated as a local equilibrium between the dissolved phase and two organic carbon sorbent phases: particles, quantified as particulate organic carbon (POC) and dissolved (colloidal) organic materials, quantified as dissolved organic carbon (DOC). The distinction between these sorbent phases was operationally defined. Particle-sorbed PCBs and POC were separated by filtration while DOC/colloid-bound PCBs and DOC were presumably unfilterable and collected with the dissolved contaminant fraction. DOC was modeled as a less effective sorbent phase than POC (Eadie *et al.* 1992, Capel and Eisenreich 1990). This was parameterized by a DOC-binding effectiveness factor (D_E), the proportionate reduction in carbon-normalized sorbent capacity of DOC relative to POC. The particle effect, the observed decrease in the partition coefficient with increasing suspended solids concentrations (O'Connor and Connolly 1980, Voice et. al. 1983), was also incorporated into the model and was parameterized by a particle interaction parameter (ν_x) (Di Toro 1985).

The phase distribution of ΣPCBs was computed from the organic carbon partition coefficient (K_{oc}), TSS and DOC concentrations, particle fraction organic carbon (f_{oc}) (f_{oc} = POC/TSS), ν_x, and D_E. A water column D_E factor of 0.01 and a sediment D_E factor of 0.1 were selected based on data presented in the literature (Eadie *et al.* 1992, Capel and Eisenreich 1990). The ΣPCB K_{oc} and ν_x were defined by calibration to dΣPCB, pΣPCB, POC, and TSS data collected at the DePere Dam. Typical log K_{oc} values for PCBs range from 5.50–7.10 L/kg (Burkhard *et al.* 1985, Swackhamer and Armstrong 1987). The ΣPCB log K_{oc} value used in the model was 6.35 L/kg. The ΣPCB ν_x value used in the model was 9.0 and reflects a weak particle effect.

The porewater diffusion rate (K_D) for dissolved and DOC-bound ΣPCBs was computed from estimates of the ΣPCB molecular diffusivity in water (D_w) and sediment porosity (ϕ) (Chapra and Reckhow 1983, Thomann and Mueller 1987). Typical values for sediment diffusion are on the order of 0.1-1.0 cm/day (Thomann and Mueller 1987). The ΣPCB K_D value used in the model was 0.40 cm/day.

The PCB volatilization rate (K_V) was computed from correlations describing the liquid and gas phase mass transfer rates in rivers and the Henry's Law constant (K_H). The liquid phase mass transfer coefficient was estimated from a modified form of the O'Connor-Dobbins reaeration correlation (O'Connor and Dobbins 1958, Smith *et al.* 1981, Mills *et al.* 1982). The gas phase mass transfer coefficient was estimated from the O'Connor-Rathbun correlation (O'Connor 1988c, Rathbun 1990). ΣPCB K_H was computed as a function of water temperature (Tateya *et al.* 1988). Typical values for PCB volatilization rates are on the order of 0.05 - 1.0 m/day (Mackay 1981, Swackhamer *et al.* 1988, Achman 1991). The ΣPCB K_V values used in the model averaged 0.16 m/day and ranged from 0.08 to 0.30 m/day.

MODEL CALIBRATION

The calibration parameters were the dispersion coefficient, the settling velocity, and the resuspension velocity. Dispersion was calibrated by constructing a chloride mass balance. Settling and resuspension were calibrated by constructing TSS and ΣPCB mass balances. The calibration approach, described below, was to systematically vary the calibration parameters within appropriate ranges and compare model predictions to field observations for each state variable. Appropriate ranges for each parameter were defined by field data or theoretical considerations. Calibration parameters were spatially or temporally varied only as justified after detailed consideration of the transport or fate process involved. This was the case for the calibration of the settling and resuspension velocities in particular. The ΣPCB mass balance is strongly dependent on the results of the sediment (TSS) transport calibration as PCBs strongly partition to suspended particles and are therefore transported by these particles. The coupled TSS and ΣPCB transport calibration approach drew heavily from the lower Fox River sediment transport research of Lick and co-workers (Gailani *et al.* 1991) and was the most significant aspect of model development.

Chloride is a conservative tracer affected only by advective and dispersive transport in the water column. The water column transport calibration required only adjustment of the dispersion coefficient because advection was defined by measured flows. Dispersion coefficients for the river segments were calibrated by comparing the predicted chloride concentration time series at the river mouth and the predicted longitudinal concentration profiles to field data. Dispersion coefficients for the inner bay segments were parameterized from the Green Bay water quality model results (Bierman *et al.* 1992). Typical dispersion coefficients estimated from theoretical or empirical relationships for rivers range from 0.5 to 100 m^2/sec (Fisher *et al.* 1979, Bowie *et al.* 1985) for rivers with morphologic characteristics similar to the lower Fox River. Calibrated dispersion coefficients in the model ranged from 0 to 75 m^2/sec, depending on flow and distance upstream of the river mouth.

Initial estimates for settling and resuspension were based on the sediment transport research of Lick and co-workers in the Fox River (Gailani *et al.* 1991) and other tributaries. This research illustrated that settling and resuspension rates vary both temporally and spatially. Resuspension, in particular, was found to be very dynamic. Resuspension fluxes increase dramatically at high flow with most sediment originating from the deeper, mid-channel portions of the river. Settling was found to vary in response to changes in the particle composition of the suspended materials (as measured by grain size distribution) and flocculation. Initial TSS settling velocities were estimated as a function of the suspended particle composition, characterized as a function of flow, and the settling rate of each particle type (sand, cohesive sediment, and biotic solids) with overall settling velocities computed as a concentration-weighted average of each particle grain size settling rate (Gailani *et al.* 1991). Initial resuspension fluxes were estimated as a function of the shear stress at the sediment-water interface (Ziegler *et al.* 1988), calculated from water velocity, and the amount of sediment entrained (Gailani *et al.* 1991) based on field measurements. Lower resuspension fluxes were specified for the net depositional sediment zones because of the lower water velocities and shear stresses in these areas.

TSS calibration defined the net solids settling flux (the difference between the settling and resuspension fluxes) and served as the basis for refining the initial settling and resuspension estimates. However, concentration measurements for two independent mass constituents are necessary to calibrate the gross settling and resuspension fluxes. The second constituent serves as a particle tracer to distinguish resuspended sediments from suspended solids originating upstream or in the watershed and allows the extent of particle interchange between the water column and sediments to be quantified. In the Fox River, PCBs serve as an excellent particle tracer as they are highly particle-associated and because the difference in PCB concentrations between the surficial sediments and water column is on the order of 5 times greater than the concentration difference for solids. Such a gradient amplifies the effect of small variations in particle transport velocities and as a result resuspension has a proportionately greater impact on particle-associated contaminant concentrations than on suspended particle concentrations. Final calibration was accomplished by adjusting the gross settling and resuspension velocities using PCB data, without altering the net settling rate defined by TSS calibration.

The calibration values for each parameter in the lower Fox River model are presented (Table 3). Also presented are values for ΣPCB physicochemical coefficients, several system parameters, and initial ΣPCB conditions in the sediments. Three parameters, the settling and resuspension velocities and the water column f_{oc}, range over several orders of magnitude. Extremely high settling and resuspension velocities occur only during high flow events and are coincident with the lowest water column f_{oc} values. The minimum settling and resuspension velocities occur at low flow while the maximum water column f_{oc} values occur during summer low flow conditions.

MODEL RESULTS

Predicted chloride, TSS, and ΣPCB time series at the Fox River mouth closely agree with the field data by visual inspection (Fig. 4). The predicted chloride, TSS, and ΣPCB concentration profiles from the DePere dam to the river mouth for the mass balance cruises were also examined and compare favorably with field data (Velleux *et al.* 1992). High flow, resuspension events dramatically affect predicted TSS and ΣPCB concentrations in the river and appear as spikes in the time series profile. Under low and even moderate flow conditions resuspension is minimal and TSS and ΣPCB concentrations decline to relatively low levels. The model predictions accurately capture the temporal variability of the field observations, both in terms of seasonal trends (summer vs. winter) and hydrologic regimes (low, medium, and high flow).

The differences between the observed and pre-

TABLE 3. Lower Fox River model calibration parameter values and other physico-chemical characteristics.

Parameter	Value or Average	Range	Units
Dispersion Coefficient, E	-	0–75	m^2/s
Settling Velocity, v_s	1.2	0.5–23.3	m/day
Resuspension Velocity, v_r	2.0×10^{-4}	$0.007–43.2 \times 10^{-4}$	m/day
Sediment Porosity, ϕ	0.78	—	—
Partition Coefficient, Log K_{oc}	6.35	—	L/kg
Particle Interaction Parameter, v_x	9.0	—	—
Binding Coefficient, Log K_B			
water column	4.35	—	L/kg
sediments	5.35	—	L/kg
Porewater Diffusion Rate, K_D	0.40	—	cm/day
Volatilization Rate, K_V	0.16	0.08– 0.30	m/day
Henry's Law Constant, K_H	3.86×10^{-4} (25°C)	$0.36–2.95 \times 10^{-4}$	atm m^3/mol
Particle f_{oc}			
water column	0.10	0.003–0.25	—
sediments	0.06	—	—
DOC concentration			
water column	8.0	—	mg/L
sediment pore water	8.0	—	mg/L
Water Temperature	10	0.4–22	°C
Wind Speed	4.5	1.14–10.64	m/sec

The burial rate was computed in the computational framework from the difference between the gross settling and gross resuspension fluxes. The depth of the surficial sediment layer changes in response the difference between the gross settling and resuspension fluxes. The Henry's Law constant (K_H) at 25°C is outside of the range of values used in the model because the water temperature did not reach 25°C.

dicted chloride, TSS, and ΣPCB concentrations at the river mouth were examined (Fig. 5). Points lying along the 45° line of the graph in Figure 5 represent perfect agreement between the data and model predictions. Some scatter about the 45° line is expected due to random error and variability in the field data as well as the model. However, the systematic divergence of points above or below this line indicates model bias. The model predictions at the river mouth for TSS and ΣPCB are generally unbiased. Regression analysis of the predictions and observations resulted in correlation coefficients (r^2) of 0.63 for ΣPCBs and 0.80 for TSS. The residual variability includes measurement errors as well as errors in predictions but does not account for any auto-correlation or minor phase delays between the observations and predictions. Both of these factors may contribute to the minor overprediction bias for low ΣPCB concentrations, as may the downstream propagation of errors in the upstream boundary condition.

To further evaluate the calibration, the cumulative frequency distributions of the observed and predicted TSS and ΣPCB concentrations at the river mouth were examined (Fig. 6). This comparison assesses the closeness with which the model reproduces the statistical properties of the data. The zero value of the inverse lognormal cumulative distribution function represents the mean value of the distribution and the slope of the line indicates the variability of the data. The predicted TSS and ΣPCB concentration distributions at the river mouth substantially agree with the frequency distributions of the field data. The slight differences between the predicted and observed means and slopes were not judged to be significant. Again, some over-prediction of ΣPCBs is apparent at low concentrations. However, this has minimal effect on export predictions which are more sensitive to the higher concentrations predicted at high flow. Agreement between the observed and predicted distributions further validates

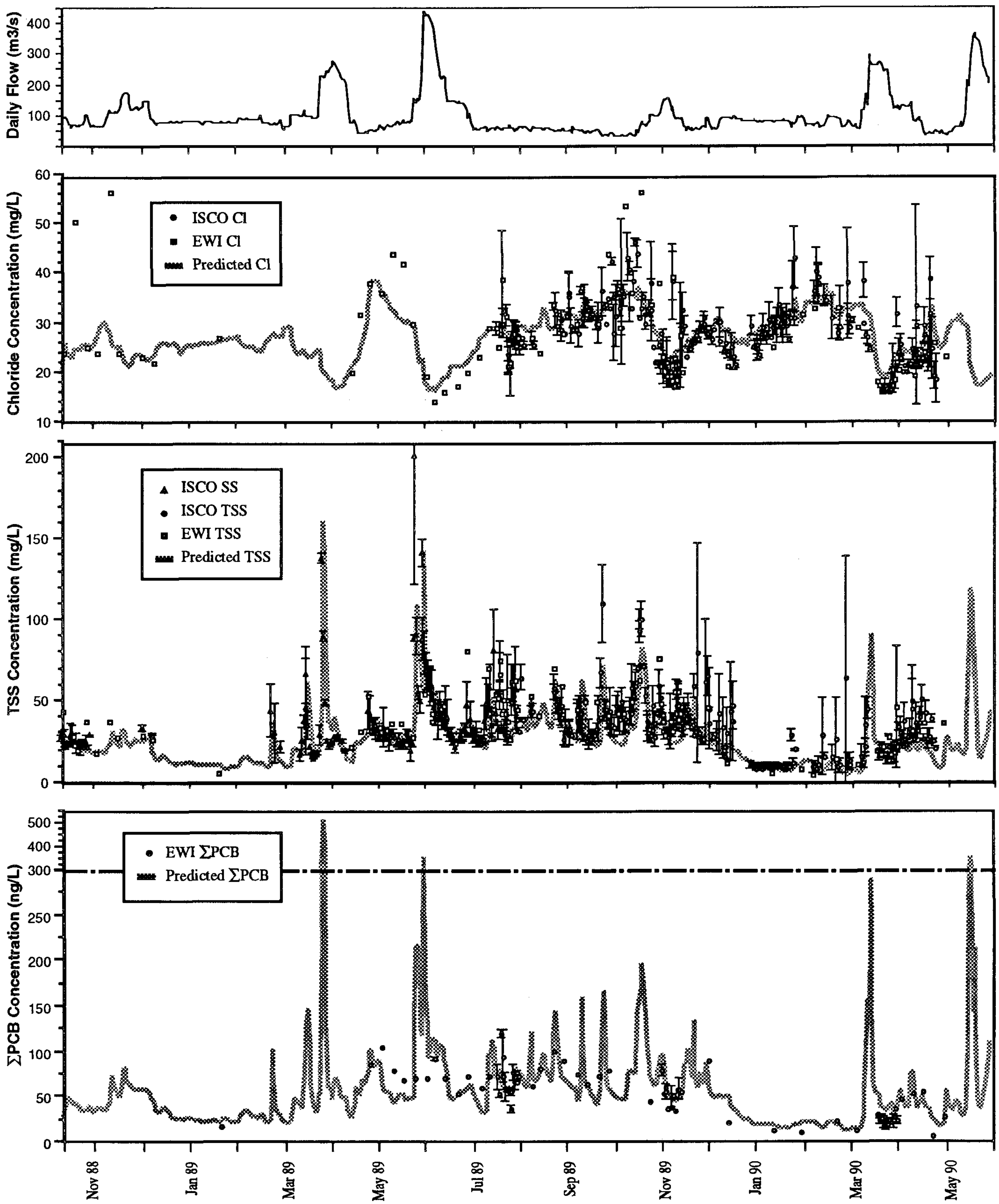

FIG. 4. Predicted and observed chloride, TSS, and ΣPCB concentrations at the Fox River mouth (error bars are ±1 standard deviation).

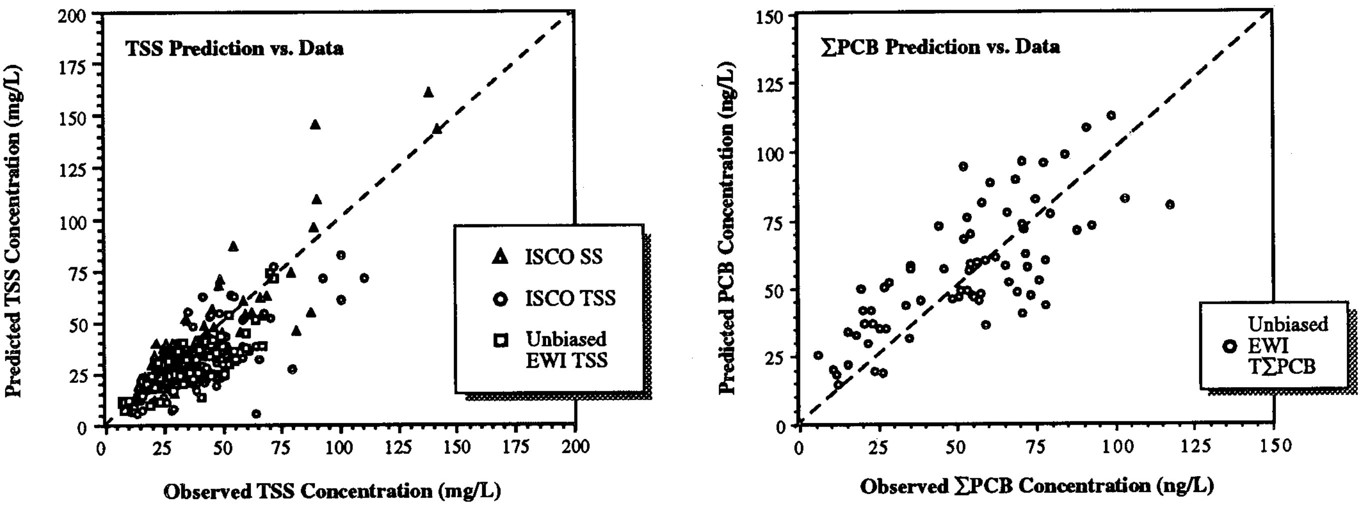

FIG. 5. TSS and ΣPCB predictions versus observations.

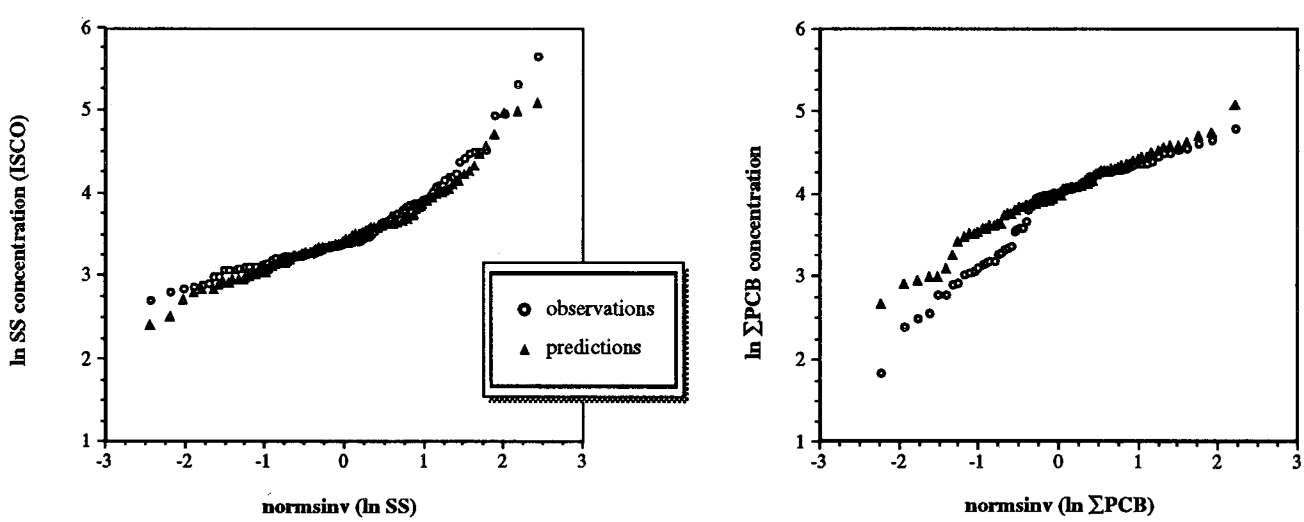

FIG. 6. Cumulative TSS and ΣPCB frequency distributions at the Fox River mouth (normsinv≡inverse normal cumulative distribution function).

the model performance across the range of environmental conditions observed during the mass balance study, including the marginal values of the field data distributions.

Unfortunately, the GBMBS data provide no direct verification of the high PCB concentrations predicted in the Fox River during high flow. In each of the four high flow events during 1989 and 1990, PCB concentrations are predicted to reach or exceed 300 ng/L (Fig. 4). However, PCBs were not monitored at these times and observed PCB concentrations exceed 100 ng/L only twice. Consequently, data collected at the Fox River mouth cannot verify a major feature of the model predictions for PCBs. As estimates, however, the high flow PCB predictions are robust. Solids data verify the net settling flux, which is approximately equal to the resuspension flux at high flow. PCB concentrations in the sediments were also measured. As sediment PCBs are sorbed to solids, the resuspension of PCBs closely follows the resuspension of solids. Therefore the predicted resuspension flux of PCBs, which substantially contributes to the PCB mass balance at high flow, is constrained by the data. High flow events, as will be shown, significantly contribute to contaminant export predictions for the Fox River.

The lower Fox River model was also applied to predict the transport and fate of PCB congeners 28+31, 56+60, 101, 138+158+163, 149, and 180 (identified by IUPAC number). The transport and fate of PCB congeners are conceptually identical to those of ΣPCBs. Upstream and point source loads, downstream boundary conditions, initial sediment conditions, and mass transfer parameter values for each congener were determined by the same procedures described for ΣPCBs (Tables 2 and 4). No additional calibration of settling and resuspension was conducted. The predicted PCB congener concentration time series at the river mouth were compared to field data (Fig. 7). As observed for ΣPCBs, high flow, resuspension events appear as spikes while concentrations decline to relatively low levels during lower flow, non-event periods in the congener time series profiles. Similarly, the congener predictions accurately describe the temporal variability of the field observations for the range of environmental conditions observed during the mass balance study. The accuracy of the model predictions for individual PCB congeners is largely the same as the model accuracy for ΣPCBs.

Estimating ΣPCB export from the Fox River to Green Bay was an important modeling objective. Daily export was computed as the sum of the predicted advective and dispersive fluxes at the river mouth. For the period 10 October 1988 to 31 May 1990 the estimated cumulative ΣPCB export to Green Bay was 423 kg (mean export of 0.71 kg/day) (Fig. 8). For calendar year 1989, the cumulative ΣPCB export estimate was 280 kg. High flow events are predicted to significantly impact contaminant export from the lower Fox River. Four high flow events occurred on the Fox River during the study period (March/April, 1989; May/June, 1989; March, 1990; and May, 1990). These events represented less than 15% of the study period yet were responsible for nearly 50% of the predicted cumulative ΣPCB export. This suggests that ΣPCB export from the Fox River is significantly related to high flow events and that much of the ΣPCB mass exported at high flows is resuspended from lower Fox River sediments.

Evaluating the sources, transport, and fate pathways for PCBs in the Fox River was another modeling objective. It is important, from both a research and a regulatory perspective, to understand both the absolute and relative magnitudes of contaminant mass fluxes. Contaminant mass fate may be evaluated directly because the mass balance model is based on the computation of mass fluxes for the most significant contaminant pathways. Cumulative ΣPCB source, transport, and fate mass fluxes for 1989 are presented in a mass fate diagram (Fig. 9). The mass fate diagram for the total mass balance (Fig. 9a) displays the cumulative ΣPCB fluxes for all modeled pathways: upstream transport, point source loading, settling and resuspension, porewater transport, volatilization, and export (advective and dispersive transport). ΣPCB export from the Fox River to Green Bay significantly exceeded

TABLE 4. Lower Fox River PCB congener model calibration parameter values.

	PCB Congener Value or Average					
Parameter	28+31	56+60	101	138+158+163	149	180
Log K_{oc} (L/kg)	6.20	6.32	6.38	6.50	6.55	6.48
v_x			9.0			
Log K_B water (L/kg)	4.20	4.32	4.38	4.50	4.55	4.48
Log K_B sediment (L/kg)	5.20	5.32	5.38	5.50	5.55	5.48
K_D (cm/day)			0.40			
K_V (m/day)	0.17	0.10	0.15	0.11	0.16	0.14
K_H (25°C) (atm m^3/mol)	2.38×10^{-4}	9.75×10^{-5}	3.23×10^{-4}	1.66×10^{-4}	4.42×10^{-4}	3.00×10^{-4}

The temperature variation of the congener K_H values was assumed to be proportional to the temperature variation of the ΣPCB K_H.

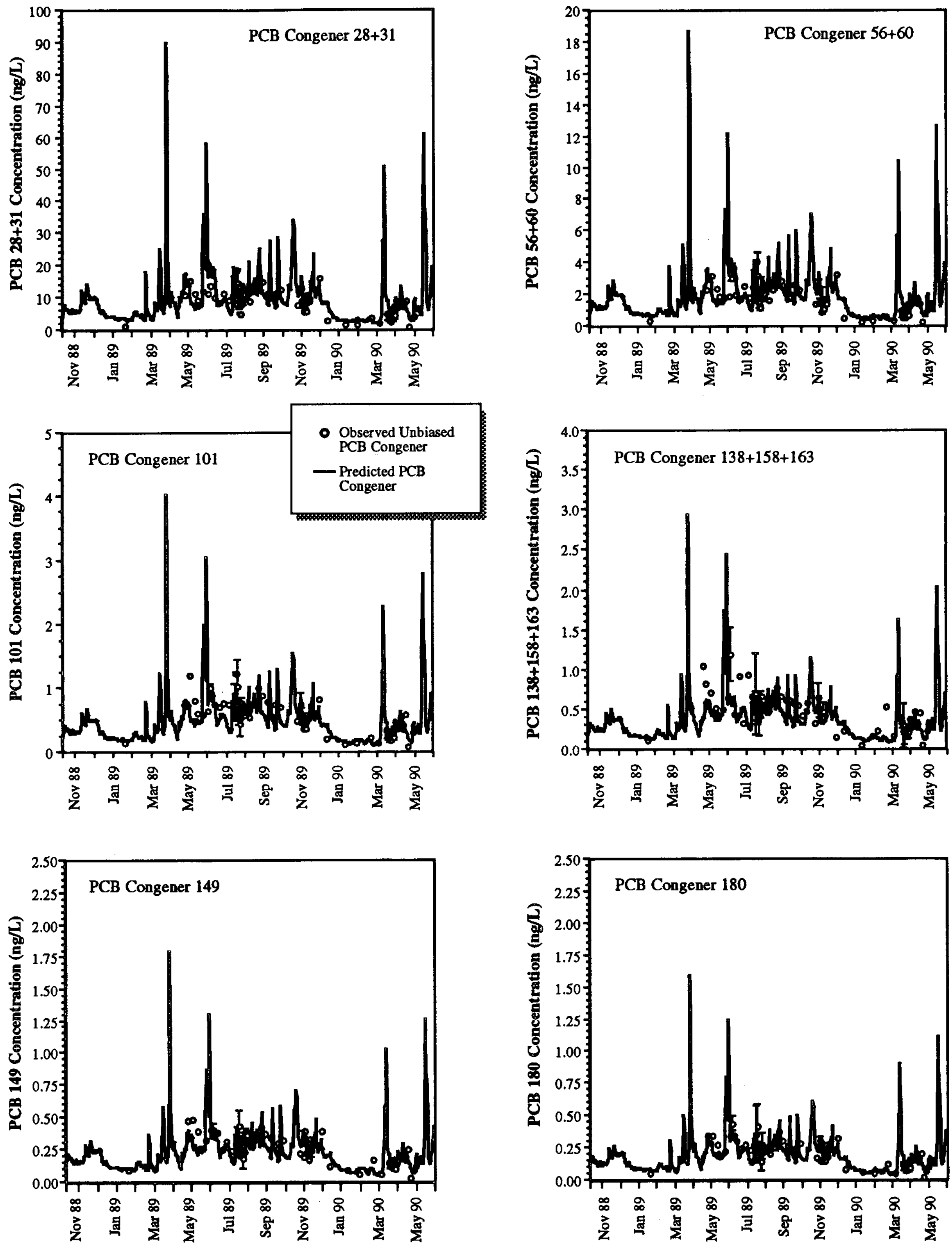

FIG. 7. Predicted PCB congener concentrations at the Fox River mouth. (Simulation begins 10 October 1988 and ends 31 May 1990.)

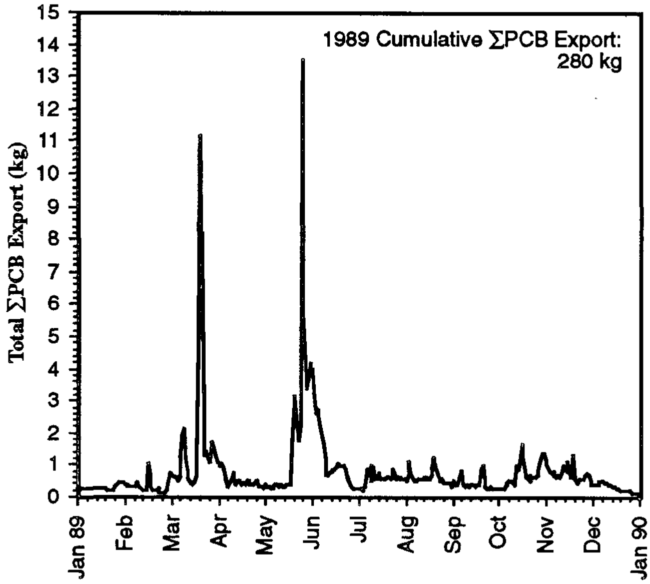

FIG. 8. Daily ΣPCB export to Green Bay for 1989 (total export = advective + dispersive transport).

upstream transport (by 106 kg, or 60%), due to the net resuspension of PCBs from the sediments. Point sources, porewater transport, and volatilization are all negligible in comparison to other PCB pathways. The origin of the PCB mass fluxes may also be evaluated by decomposing the source terms in the model because the mass balance equations are linear and their solution may be separated into components. This allows each source to be analyzed independently and its significance assessed. For PCBs originating from the upstream watershed (Fig. 9b), only 60% were exported to Green Bay in 1989; the remaining mass entered the sediments. For PCBs initially contained in the lower River sediments (Fig. 9c), 80% of the resuspended mass was exported to the Bay in 1989. A comparison of these two sources shows that more than half (60%) of the ΣPCB export in 1989 originated from the PCB mass present in the lower river sediments.

By comparing the magnitude of ΣPCB fate pathways, the relative importance and sensitivity of the transport and fate parameters to the predicted ΣPCB export at the river mouth can be assessed. The cycling of solids between the water column and sediments is the most significant ΣPCB fate pathway and the model is most sensitive to variations of parameters that affect sediment-water interactions: the settling and resuspension rates and the partition coefficient. Relative to other processes, the ΣPCB mass cycled between the water column and sediments is large. Due to the five-fold difference that exists between the ΣPCB concentrations on the particles in the water column and sediment, variation of the gross settling and resuspension rates (assuming that the net TSS settling rate remains constant) results in large differences in the predicted ΣPCB export at the river mouth, especially during high flows when water column-sediment interaction is at a maximum. Due to the strong association of PCBs with particles, variation of the partition coefficient also results in large differences in the predicted ΣPCB export at the river mouth.

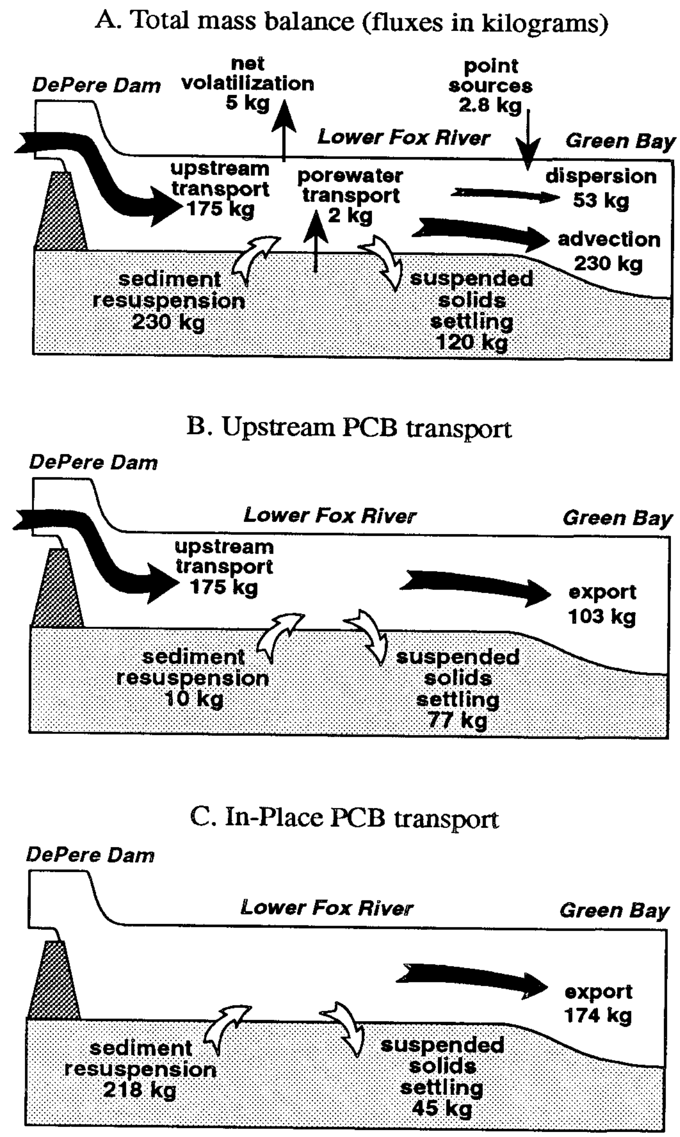

FIG. 9. ΣPCB mass fate in the Lower Fox River: 1 January to 31 December 1989.

Parameterization of sediment resuspension fluxes was a fundamental challenge of the lower Fox River model development. Ideally, resuspension could be modeled as a function of flow, based on a shear stress relationship. Examination of the calibrated resuspension velocities as a function of measured flow (Fig. 10) reveals the general features of such a relationship as well as substantial unexplained variability. At high flow, the calibration shows the power law dependence of resuspension on flow suggested by process research (Zeigler *et al.* 1988) indicating that the resuspension flux is proportional to the third power of shear stress, or the sixth power of water velocity, once a critical shear is exceeded. At low flow, however, the calibrated resuspension velocities are generally small (less than 0.1 mm/day) but still significant. This "background" resuspension substantially influences water column PCB concentrations but has little impact on solids concentrations. This is because the difference in PCB concentrations between the surficial sediments and water column is greater then the concentration difference for solids. The residual variability in the resuspension velocities, evident as scatter in Figure 10, is related to factors not resolved in this model. These factors include sediment bed compaction and armoring, spatial variability in sediment resuspension properties, variation in the shear stress at the sediment-water interface due to non-uniform flow distributions, short-term changes in water levels (seiche action), wind and wave effects, and possible other factors.

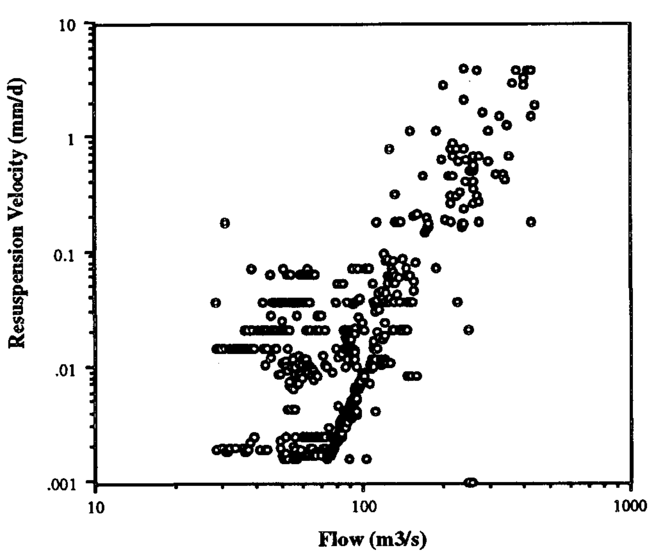

FIG. 10. ***Calibrated resuspension velocities versus flow in the lower Fox River model (upstream erosional sediment zone).***

It is possible that some mechanism other than resuspension releases PCBs from the sediments under low flow conditions. However, there is no evidence to support this. Nonpoint, landfill, and groundwater contaminant sources along the lower Fox River were assessed as part of the GBMBS. None of these sources even approach being significant contributors of PCBs to the water column mass balance. Given that the flux of PCBs released from the sediments by background resuspension is at least one order of magnitude greater than the sum of all other diffuse sources, resuspension is the most likely mechanism for PCB release at low flow.

DISCUSSION

PCB transport in the lower Fox River is highly non-conservative due to the strong association of PCBs with particles. In this system, particles are extensively cycled between the water column and sediments. As a result, much of the ΣPCB mass entering the lower river from over the DePere Dam in 1989 did not reach the river mouth. Sediment resuspension is the single greatest factor influencing ΣPCB export to Green Bay. The in-place ΣPCB mass resuspended and exported to Green Bay was as large as the upstream import. This is clearly illustrated (Fig. 9) by noting that without the resuspension of lower river sediments, only 103 kg of ΣPCBs would have been exported to Green Bay in 1989. ΣPCB export is also event responsive. Nearly half of the cumulative ΣPCB export to Green Bay was transported during high flow events; ΣPCB transport increases when particle transport increases. Further, the in-place sediment ΣPCB reservoir is very large; the total ΣPCB inventory in 1990 was 30,000 kg (with more than 22,000 kg stored in the modeled sediments). Although nearly 200 kg of ΣPCBs were exported from the sediments during 1989, this represents less than 1% of the total ΣPCB inventory of the lower river.

The goal of water quality modeling efforts is usually to relate loadings from tributaries and other sources to concentrations and exposures in a receiving waterbody. The lower Fox River modeling effort was unique in that a mass balance approach was applied to estimate tributary loads to a receiving waterbody. Tributary loads are typically estimated by statistical approaches (Dolan *et al.* 1981, Preston *et al.* 1989). Given the interactions between the river and bay, to statistically estimate tributary loads from the Fox River samples would typically be collected above the DePere Dam to avoid the dilution of river water by intruding water from Green Bay. Estimates based on such sampling would be much lower than the predicted tributary load as they would not account for contaminant resuspension from lower Fox River sediments. The model results clearly demonstrate this: the export at the river mouth was 280 kg while the import over the DePere Dam was 174 kg. Additionally, mass balance water quality models can rationally predict concentrations and loads during unmonitored periods, such as high flow events, when sampling for trace contaminants such as PCBs may not be feasible. Since high flow events transport significant portions of the total loading, the mass balance approach offers an improved means for estimating contaminant export to receiving waterbodies from tributaries with significant in-place pollutant reservoirs.

The GBMBS offered an initial opportunity to model PCB transport and fate on the congener level. The project focus on ΣPCBs was motivated by the need to relate model predictions to regulatory endpoints: water and sediment quality criteria, fish consumption criteria, and discharge permits, all of which are expressed in terms of total PCB concentrations. However, the mass balance approach may also be applied for individual congeners. The congeners examined were selected based on predominance in the water column, sediments, and biota of the river and bay with physicochemical properties spanning a representative range of PCB hydrophobicities and volatilities. As for ΣPCBs, mass fate diagrams could be constructed and the differential transport and fate characteristics of each congener identified. Not only do the congener results provide a qualitative confirmation of the model, but they also demonstrate that the mass balance modeling approach may be successfully applied at the congener level.

Given sufficient and appropriate data, the mass balance approach can be used to successfully develop quantitative models describing contaminant export from tributaries to receiving waterbodies. The mass balance approach can be used to evaluate the importance of in-place pollutants and the significance of high flow events to contaminant export. The lower Fox application demonstrated both the strengths and limitations of the mass balance approach as a tool for assessing in-place pollutant export. The strength of the approach is that it is data driven and therefore intrinsically consistent with field observations and allows quantitative cause-effect relationships between contaminant sources and water quality to be established. With appropriate data, the magnitude and dynamics of contaminant transport and fate pathways can be accurately defined. The limitation of the approach is that it requires large, comprehensive data sets and that it is often technically and logistically difficult, and therefore expensive, to collect data that accurately define contaminant transport and fate. Despite the extensive data requirement, there appears to be no other alternative to the mass balance approach to quantitatively assess and predict contaminant transport and fate as well as the relationship between loads and concentrations. Without the necessary verification data, model predictions may be uncertain. However, the data requirements of this model are quite specific. The critical lesson for planning future monitoring efforts of tributaries with significant in-place pollutant reservoirs is that the maximum exports are predicted to occur at high flow when TSS concentrations are high. With respect to the Fox River, PCB concentration data (in addition to TSS data) are needed during high flow periods to verify the PCB export predictions and reduce model prediction uncertainty.

CONCLUSIONS

A mass balance approach was used to model daily contaminant cycling in the lower Fox River from the DePere Dam to Green Bay. The cumulative ΣPCB export from the Fox River to Green Bay was 280 kg for calendar year 1989. For the mass balance period 10 October 1988 to 31 May 1990 the export was 423 kg. Nearly 50% of the cumulative ΣPCB mass exported to Green Bay was delivered by four high flow events during the mass balance period. The sediments of the lower Fox River between the DePere Dam and the river mouth are a significant source of ΣPCBs to Green Bay. The ΣPCB mass exported to the bay is much (60%) greater than the mass entering from the upstream watershed. As a result of high flow events, the sediments of the lower Fox River are intensely cycled and release ΣPCBs from the in-place reservoir. Present industrial and municipal point source ΣPCB inputs are negligibly small in comparison to other sources.

The mass balance approach has been demonstrated to offer highly accurate predictions of PCB export from the Fox River. Given appropriate field data, this approach may be expected to provide similarly accurate results for other contaminants and other tributary systems. The mass balance approach also offers potential advantages over statistical methods for estimating tributary loads in terms of accuracy, temporal resolution, overcoming logistical problems associated with sampling complex systems, and identifying the critical processes contributing to variability in contaminant concentrations and loads. Perhaps the greatest value of the mass balance approach to the lower Fox River study was as an assessment tool to focus concern (research as well as remediation efforts) on the relationship between sediment transport and contaminant fate to directly improve predictive tools for evaluating in-place pollutant issues in the Fox River and elsewhere.

The lower Fox River modeling effort identified the importance and quantified the extent of resuspension processes to PCB transport in the lower Fox River and export to Green Bay. The principal unanswered issue in the lower Fox River is the long-term fate of the 30,000 kg PCB inventory of the sediments. It remains unknown if this in-place reservoir is transportable by future high flow events or whether these sediments can be effectively remediated. Further field data collection and modeling efforts are underway to address these issues in the Fox River, based on improved water quality modeling techniques and more resolved sediment data.

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